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(54) Name of the invention: Thermally Expandable Ceramic Fiber Composite Material

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Patent Assignee: Nippon Pillar Kogyo Company

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*[Note: Names, addresses, Company names and brand names are translated in the most common manner. Japanese language does not have singular or plural words unless otherwise specified with numeral prefix or general form of plurality suffix. Translator's note.*

**(54) [Name of the invention]**

**Thermally expandable ceramic fiber composite material**

**[Range of the claims of the invention]**

[Claim 1]

Thermally expandable ceramic fiber composite material characterized by the fact that it is provided with a thermally expandable layer that has as its main material a vermiculite ore material as a thermally expandable material, and with a ceramic filter, that is at least placed on the above described thermally expandable layer that has ceramic fiber as its main material, or a heat insulating layer that is placed on the side of the surface that is the catalyst contact surface, and also, the thickness of the above described heat insulating layer is defined in the range of 20 % ~ 70 % of the thickness of the total body.

[Claim 2]

Thermally expandable ceramic composite material according to the above described Claim 1 of the present invention where the thickness of the above described thermally expandable layer is defined as being in the range of 30 % ~ 80 % of the thickness of the total body.

**[Simple explanation of the invention]**

[0001]

**[Technological sphere of application]**

The present invention is an invention about a thermally expandable ceramic composite material that is used in the ceramic filters used in automobiles or the

ceramic catalyst support materials, etc.

[0002]

[Previous technology]

For example, in the pipelines for the exhaust gases in the automobiles, in order to reduce etc., clean up the nitrogen oxides that are inside the exhaust gases, a ceramic filer or ceramic catalyst are used. In order to support this ceramic catalyst etc., in the exhaust gas pipelines, in the past, a material from ceramic fiber has been used as the substrate material, and as the thermally expandable layer, a support material has been used that has been formed from a mat shape thermally expandable ceramic fiber composite material, that has been prepared as a small amount of vermiculite and a small amount of an organic binder material have been spread out.

[0003]

**[Problems solved by the present invention]**

However, at the time when inside the above described ceramic filter or ceramic catalyst, exhaust gas burns again, because of the heat of the reaction, the temperature of the ceramic filter or the ceramic catalyst \is increased to a temperature in the range of 800 ~ 1000oC. In the case of the support materials according to the previous technology that has vermiculite ore material as its main structural material, if it is heated, it expands and if the vermiculite ore material is exposed to high temperatures in the range of 800 ~ 1000oC, it shows shrinkage properties, and there is the trend that in the high temperature region, the supporting properties relative to the ceramic catalyst etc., are deteriorated. And if in this state it endures vibrations or friction, it is easy for a pulverization to occur and for a powder type material to be separated from the layer shape state material, and as a result from that this causes shape change in the case of the above described ceramic filter or ceramic catalyst material, and there has been the danger that a blow through the supporting material would occur.

[0004]

In the case of the present invention, in order to solve problems such as those described here above, it is an invention that has as a goal to suggest a thermally expandable ceramic fiber composite material where the exposure of the vermiculite compounded layer to high temperatures of 800oC or above, is eliminated, and even at the time of use at the high temperature region, it is a material that can sustain a stable supporting force relative to a ceramic filter or ceramic catalyst material.

[0005]

[Measures in order to solve the problems]

In order to achieve the above described goal, the thermally expandable ceramic composite material according to the present invention is a material that it is provided with a thermally expandable layer that has as its main material a vermiculite ore material as a thermally expandable material, and with a ceramic filter, that is at least placed on the above described thermally expandable layer that has ceramic fiber as its main material, or a heat insulating layer that is placed on the side of the surface that is the catalyst contact surface, <u>and also, the thickness of the above described heat insulating layer is defined in the range of 20 % ~ 70 % of the thickness of the total body.</u>

[0006]

<u>Regarding the above described thermally expandable ceramic composite material, it is preferred that</u> the thickness of the above described thermally expandable layer <u>is defined</u> as being in the range of 30 % ~ 80 % of the thickness of the total body.

[0007]

**[Effect]**

According to the present invention, regarding the proportion of the heat insulating layer, that has as its main material a ceramic fiber, and that is placed on the thermally expandable layer provided at least on the side that is contacting the ceramic filter or the ceramic catalyst, when the 800 ~ 1400oC range of temperatures during the usage is assumed, at a temperature of 800oC it is defined as 20 %, at a temperature of 1000oC it is defined as 30 %, at a temperature of 1200oC it is defined as 50 %, and at a temperature of 1400oC it is defined as 70 %, and it is conveniently determined in correspondence with the temperature of the usage. And because of that, even when because of the heat of reaction, the ceramic filter or the ceramic catalyst are heated at high temperatures in the range of 800 ~ <u>14</u>00oC, it is possible to control the temperature of the above described thermally expandable layer, <u>that has vermiculite as its main material</u> to a temperature that is less than 800oC. Consequently, the decrease of the supporting force relative to the above described ceramic filter or ceramic catalyst material that accompanies the shrinkage properties when the vermiculite ore material, that is the main structural material of the above described thermally expandable layer, is exposed to high temperatures of 800oC or above, is eliminated, and even at the time when it is used at the high temperature region, there is no shape change of the ceramic catalyst etc., blow through etc., and it is possible to have a stable support.

[0008]

Especially, if the thickness of the <u>above described thermally</u> expandable layer is

defined as being in the range of 30 ~ 80 % of the thickness of the total body, it is possible to reliably obtain a constant supporting force.

[0009]

[Practical Examples]

Here below, the practical implementation examples according to the present invention will be explained based on the diagrams shown. Figure 1 represents one part of a sectional view diagram showing the use of the thermally expandable ceramic composite material according to one practical example of the present invention, as a supporting material for a ceramic filter or a ceramic catalyst used in automobiles.

[0010]

In Figure 1, 1 represents the thermally expandable layer, 2 represents the heat insulating layer that has ceramic fiber as its main material, and the two layer structure of the thermally expandable ceramic fiber composite material 3 has a structure that is formed from both 1 and 2 above. The above described heat insulating layer 2 is placed on the thermally expandable layer 1, and it is laminated as a layer on at least on the side of the surface that is in contact with the ceramic filter or the ceramic catalyst material 4.

[0011]

The structure of the above described thermally expandable layer 1 and the heat insulating layer 2 is explained as according to the illustrated in Figure 2. First, the spreading solution A, that has a concentration of 1.5 weight % of a material that has a compounding ratio such that it contains 83 weight % of ceramic fiber, 5 weight % of sepiolite ore material, and 12 weight % of organic binder material, is prepared as the heat insulating layer. Also, the spreading solution B, that has a concentration of 1.5 weight % of a material that has a compounding ratio such that it contains 30 weight % of ceramic fiber, 4 weight % of sepiolite ore material, and 54 weight % of vermiculite ore material, is prepared as the thermally expandable layer.

[0012]

Here, the preferred compounding ratios of the materials that form the structure of the above described heat insulating layer 2 and thermally expandable layer 1, are according to the presented in Figure 2. regarding the heat insulating layer 2, because it has as its main material a ceramic fiber that has thermal resistance properties and heat insulating properties, in the case when the content of the ceramic fiber material is less than 60 weight %, the thermal resistance properties and the heat insulation properties are insufficient, and in the case when the contained amount exceeds 95

weight %, the compounded amount of the organic binder material becomes too small, and it becomes impossible to shape the material in a sheet type shape. regarding the sepiolite ore material, even if it is not added the main effect as a heat insulating layer is not lost, however, it is a so-called inorganic bonding material, and by adding it in a small amount it is possible to reinforce the thermal resistance effect. However, in the case when the added amount exceeds 10 weight %, the compounding ratio of the ceramic fiber material is decreased, and the heat insulating properties of the mat are decreased and together with that because the sepiolite ore material has the effect as a bonding material where at the time when the material is under a high temperature condition, it is bonded with the fiber material and forms one body, the mat density is increased and the porosity is decreased. Consequently, the porosity inside the mat that disturbs the heat transfer, is decreased and the heat insulating properties are lost.

[0013]

Also, regarding the heat insulating layer 2, because the expansion specific properties are not its main goal, even though there are times when vermiculite is not used, in the case when as a whole mat body it is required that after a time at a low temperature it has a large amount of expansion, vermiculite ore material is added in an amount of up to 30 weight %, and by that the initial period expansion properties can be increased. However, in the case when the compounded amount of vermiculite exceeds 30 weight %, the thermal deterioration ratio of the heat insulating layer becomes large and the supporting force relative to the ceramic catalyst etc., is decreased. Regarding the organic binder material, after the spreading it is absorbed in the mat and because of that a minimum of 1 ~ 2 weight % is necessary, and if the amount exceeds 20 weight %, the thermal resistance properties of the mat are decreased.

[0014]

Then, regarding the thickness of the heat insulating layer 2, as it is shown according to the presented in Figure 3, in order that following the catalyst use temperatures, the temperature of the thermally expandable layer 1 is controlled so that it does not exceed 800oC, it is correspondingly set in the range of 20 ~ 70 %. And namely, the proportion of the heat insulation layer 2 relative to the thickness of the whole body of the thermally expandable ceramic fiber composite material 3 is conveniently defined in correspondence with the temperature during the usage, so that when a temperature range of 800 ~ 1400oC usage temperature range is assumed, at a temperature of 800oC it is 20 %, at a temperature of 1000oC it is 30 %, at a temperature of 1200oC it is 50 %, at a temperature of 1400oC it is 70 %. Also, regarding the thickness of the thermally expandable layer 1, from the supporting force that is required relative to the ceramic catalyst material, it is defined as being in the range of 30 ~ 80 % relative to the total thickness of the thermally expandable ceramic fiber composite material 3.

[0015]

In the thermally expandable layer 1, in order to increase the compounding ratio of the vermiculite ore material that shows additional thermal expansion properties, it is a good option if the fiber material is used in an amount that is in the range of 10 ~ 60 weight %. In the case when that amount is less than 10 weight %, as a base material, the thermal resistance properties are decreased too much, and in the case when that compounding ratio exceeds 60 weight %, the expansion properties are decreased. By the addition of a small amount of sepiolite ore material, it is possible to obtain an improved thermal resistance reinforcement effect, however, in the case when the compounded amount exceeds 10 weight %, the compounding ratio of the ceramic fiber material becomes too small, and the fundamental heat insulating properties of the mat are deteriorated and together with that because the sepiolite ore material has the effect as a bonding material where at the time when the material is under a high temperature condition, it is bonded with the fiber material and forms one body, the mat density is increased and the porosity is decreased. Consequently, the porosity inside the mat that disturbs the heat transfer, is decreased and the heat insulating properties are lost.

[0016]

In the case when the compounded amount of the vermiculite ore material is less than 30 weight %, the expansion properties are unsatisfactory, and in the case when that amount exceeds 90 weight %, the compounded amounts of the fiber base material and the bonding material, are decreased, and problems are caused in the mat preparation, and together with that at the time at a high temperature, the whole amount of the organic binder material is burned and lost and because of that the initial shape is not preserved and a significant drop in the strength is caused. Regarding the organic binder material, in order to improve the exploitation properties after the preparation of the mat a minimal amount in the range of 1 ~ 2 weight % is necessary, however, if the amount used exceeds 20 weight %, the thermal resistance properties of the mat are reduced.

[0017]

On the other hand, as the spreading solution C with a concentration of 1.5 weight % of a material obtained by the mixing of 19 weight % of ceramic fiber, 71 weight % of vermiculite ore material, 10 weight % of organic binder material, is prepared to be used as the thermally expandable layer, and then, the spreading solution D with a concentration of 1.5 weight % of a material obtained by the mixing of 70 weight % of ceramic fiber, 20 weight % of vermiculite ore material, 10 weight % of organic binder material, is prepared to be used as the heat insulating layer.

[0018]

As the above described ceramic fiber, alumina silicic acid salt, for example SC 126OD2 (commercial name, manufactured by Shinnichi tetsu Kagaku Company) is used, as the vermiculite ore material, non expanded vermiculite number 0, treated with ammonium sodium hydrophosphate is used, as the sepiolite ore material, Mirukon MS-2-2 (commercial name, manufactured by Showa Mining Company) is used, as the organic binder material, Sumica Flex 900 (commercial name, manufactured by Sumitomo Chemical) is used;

[0019]

The above described spreading solutions A and B are used and as the Practical Example 1, the method for the manufacturing of the thermally expandable ceramic fiber composite material, is explained. First, as it is shown according to the presented in Figure 4, the bottom opening spreading bucket 13 is prepared, that has the spreading net 11 and the barrier plate 12, that is positioned on the top of that and that can be slipped on and off. In this spreading bucket 13 25 liters of the above described spreading solution A are introduced, and after that the barrier plate 12 is placed in between and 50 liters of the spreading solution B are introduced so that the surface level of the spreading solution A is not disturbed. After that the above described barrier plate is gently pulled out and then after that a water extraction is conducted and the heat insulating layer 2, that corresponds to the above described spreading solution A and the thermally expandable layer 1, that corresponds to the above described spreading solution B, are spread and combined and a spread material is prepared. After that, this spread material is dried, pressed and by that a thermally expandable ceramic fiber material 3 is manufactured that has a thickness of 5 mm and a weight per surface area of 5000/m2.

[0020]

By using the above described spreading solutions C and D, as the Practical Example 2, the method for the manufacturing of the thermally expandable ceramic fiber composite material, is explained. First, 25 liters of the spreading solution D (both solutions are D, probably is a C and is an error - translator's note) are introduced and poured into the above described spreading bucket 13, and after that the barrier plate 12 is introduced in between and then 50 liters of the spreading solution D are poured so that the surface level of the spreading solution C is not disturbed. After that the above described barrier plate is gently pulled out and then after that a water extraction is conducted and the heat insulating layer 2, that corresponds to the above described spreading solution D and the thermally expandable layer 1, that corresponds to the above described spreading solution C, are spread and combined and a spread material is prepared. After that, this spread material is dried, pressed and by that a thermally expandable ceramic fiber material 3 is manufactured that has a thickness of 5 mm and a weight per surface area of 5000/m2.

[0021]

Then, by using the above described spreading solution B, a thermally expandable ceramic fiber composite material is manufactured that is used as a reference example. In other words, 75 liters of the above described spreading solution B is introduced and filled in the above described spreading bucket 13 and after that it is water extracted and by that a thermally expandable material was obtained. This was then dried and pressed and by that a thermally expandable ceramic fiber material is manufactured that has a thickness of 5 mm and a weight per surface area of 5000/m2.

[0022]

Each of the thermally expandable ceramic fiber composite materials obtained according to the above described Practical Example 1 and Practical Example 2, are correspondingly wrapped around a ceramic catalyst 4, so that the side of the heat insulating layer 2 is the inner side, and after that, as it is shown according to the presented in Figure 5, on those the casing 14, that is manufactured from SUS 304, is placed and they are covered, and by that the catalyst assembly product was manufactured. The same way, the manufactured as a reference example, thermally expandable ceramic fiber composite material is wrapped around a ceramic catalyst and after that it is covered with a casing and by that the catalyst assembly product was manufactured.

[0023]

After that, each of the catalyst assembly products obtained according to the above described Practical Examples 1 and 2, and together with that the catalyst assembly product used as the reference example, were subjected to thermal tests by using the thermal testing equipment that is provided with a thermocouple 15 and gas burners 16 and 17, as shown according to the presented in Figure 6. Namely, the outer periphery side of the ceramic catalyst 4 in each of the catalyst assembly products is heated by using the gas burners 16 and 17, so that the temperature becomes 1000oC, and it is maintained in this heated state for a period of 3 hours.

[0024]

After the above described heating for a period of 3 hours, it is cooled and then after that by using the supporting force measurement device presented according to Figure 7, the supporting force relative to the ceramic catalyst 4, was measured. In other words, for each of the above described catalyst assembly products the supporting force relative to the ceramic catalyst 4, is measured through a load cell 19, in the state where they are supported on a removable pipe 18, and at the compression rate of 50 mm/minute.

[0025]

After that, each of the above described catalyst assembly products is supported on a vibrating container 20 of the vibration testing equipment shown according to Figure 8, and vibration with a vibration amplitude of 20 mm and a vibration frequency of 290 back and forth/ minute, is applied, and this is maintained for a period of 3 hours, and after that again, the same way as it has been described here above, the supporting strength was measured. The supporting force after the vibration experiment is presented according to Figure 9, where the supporting force after the heating has been taken as 100.

[0026]

As it also becomes clear from the supporting force index according to Figure 9, in the case of the material according to the reference example, the shrinkage ratio of the vermiculite that is contained in the thermally expandable layer is high, and by the vibrational testing the state of the layer shape is destroyed and it is pulverized to a powder type material and the degree of the decrease of the supporting force is significant. Contrary to that, in the case of the materials according to the Practical Examples 1 and 2, because they are materials that have a heat insulating layer 2, that has ceramic fiber as its main material, the decrease of the expansion force due to the shrinkage of the vermiculite ore material that is contained in the thermally expandable layer, can be controlled and suppressed, and because of that, it is understood that even after the vibration test, the state of the layer shape is effectively maintained.

[0027]

Moreover, in the case of the above described thermally expandable ceramic fiber composite material 3, because of the fact that it is a material where a thermally expandable layer 1 and a heat insulating layer 2 are unified as one body as their spreading solutions are spread and combined, there is no addition of time and labor for the assembly, and the manufacturing is easy. However, it is also possible to have a composite material that has a structure that is formed as the thermally expandable layer 1 and the heat insulating layer 2 are separately spread and dried and then after that they are pressed and the pressure adhesion of both of these is accomplished.

[0028]

Also, regarding the above described heat insulating layer 2, it is also a good option if it is provided not only on the side that is in contact with the ceramic filter or the ceramic catalyst 4 on the above described thermally expandable layer 1, but also, as it is shown according to the presented in Figure 10, it is provided on the side of the opposite surface.

[0029]

[Results from the present invention]

According to the above described, in the case of the present invention, a composite material is prepared that has a two layer structure, such that it is provided with a thermally expandable layer, that has vermiculite ore material as its main structural component, and a heat insulating layer, that is provided on the above described thermally expandable layer, at least on the side of the surface that is in contact with the ceramic filter or the ceramic catalyst, and that is a layer that uses ceramic fiber as its main material, and also, it is such a structure where the thickness of the above described heat insulating layer is defined in the range of 20 % ~ 70 % relative to the thickness of the total body; and by that it is a material where even if the ceramic filter or the ceramic catalyst becomes heated to a high temperature in the range of 800 ~ 1400oC because of the heat of the reaction, it is possible to control and suppress the heating so that the temperature to which the above described thermally expandable layer that has vermiculite ore material as its main component is exposed is less than 800oC. Consequently, it is possible to eliminate the decrease of the expansion force of the thermally expandable layer obtained due to the shrinkage properties of the vermiculite ore material, that is the main component of the thermally expandable layer, and even at the time when it is used in the high temperature region, at temperatures exceeding 800oC, it is a material where the supporting force relative to ceramic catalyst etc., is very stable and is reliably maintained.

[0030]

Especially, when as in the claim 2, the thickness of the thermally expandable layer is defined in the range of 30 ~ 80 % relative to the thickness of the total body, by that, it is possible to obtain a material that demonstrates a supporting force relative to ceramic catalysts etc., at the time of use at the high temperature region, that is even more stable and more reliably maintained.

**[Simple explanation of the figures]**

[Figure 1]

Figure 1 represents one part of a sectional view diagram showing the use of the thermally expandable ceramic composite material according to the practical example of the present invention, as a supporting material for a ceramic filter or a ceramic catalyst used in automobiles.

[Figure 2]

Figure 2 is a table that shows the compounding of the spreading solutions of the

thermally expandable ceramic fiber composite material.

[Figure 3]

Figure 3 is a table representing the range of the thickness of the heat insulating layer relative to the temperature of use of the catalyst.

[Figure 4]

Figure 4 represents a structural diagram of the spreading bucket that is used at the time of the manufacturing of the thermally expandable ceramic fiber composite material.

[Figure 5]

Figure 5 is an outside view diagram showing the catalyst assembly product.

[Figure 6]

Figure 6 represents a structural diagram showing the heating test equipment relative to the catalyst assembly product.

[Figure 7]

Figure 7 is a structural diagram showing the equipment for the measurement of the supporting force relative to the catalyst assembly product.

[Figure 8]

Figure 8 is a structural diagram showing the vibration test equipment relative to the catalyst assembly product.

[Figure 9]

Figure 9 is a table showing the supporting force index after the vibrational test.

[Figure 10]

Figure 10 is a diagram that shows another structure of the thermally expandable ceramic fiber composite material.

**[Explanation of the symbols]**

1.......thermally expandable layer
2.......heat insulating layer

4......ceramic filter or ceramic catalyst

In Figure 3:
1. temperature of use of the catalyst, 2. ratio of the layer thickness

In Figure 9:
1. supporting force index after the vibration test, 2. Practical Example 1, 3. Practical Example 2, 4. reference Example.

Figure 2:
1. Spreading solutions compounding, 2. Practical Example 1, 3. Practical Example 2, 4. reference example, 5. spreading solutions, 6. spreading solution A (used for the heat insulating layer), 7. spreading solution B (used for the thermally expandable layer), 8. spreading solution C (used for the thermally expandable layer), 9. spreading solution D (used for the heat insulating layer), 10. heat insulating layer, 11. thermally expandable layer, 12. ceramic fiber, 13. sepiolite ore material, 14. vermiculite ore material, 15. organic binder material, 16. spreading solution concentration, 17. reference example

Figure 8:
vibrations

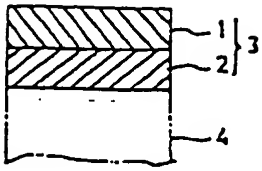
Figure 7:
compression rate 50 mm/minute

Figure 4:
1. spreading solution

**Patent Assignee: Nippon Pillar Kogyo**

*Translated by Albena Blagev ((651) 735-1461 (h), (651) 704-7946 (w))*
*1/23/99*

【図1】




1：熱膨張層
2：断熱層
4：セラミックフィルタ あるいは セラミック触媒

【図3】

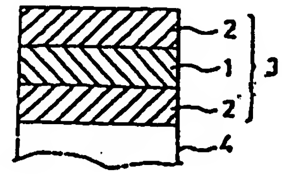
| | | | | | |
|---|---|---|---|---|---|
| 1 | 触媒使用温度 | 800℃ | 1000℃ | 1200℃ | 1400℃ |
| 2 | 層の厚さの比率 | 20% | 30% | 50% | 70% |

【図9】

1 振動試験後の保持力指数

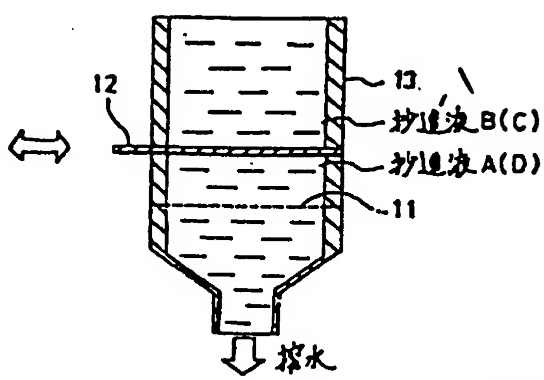
| | | | |
|---|---|---|---|
| 2 | 実施例1 | 3 実施例2 | 4 比較例 |
| | 80 | 70 | 50 |

【図10】






【図4】



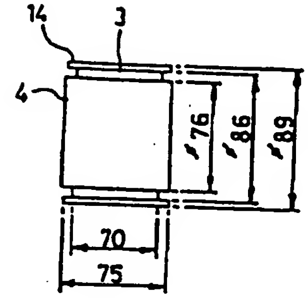
【図2】

1 抄造液の配合

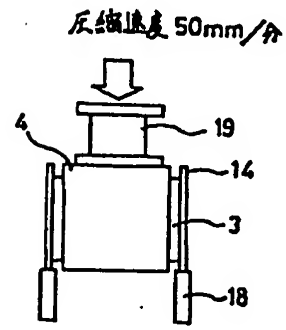
| 5 抄造液 | 2 実施例 1 (Ex.) | | 3 実施例 2 (Ex.) | | 4 好ましい配合量 (Preferred) | |
|---|---|---|---|---|---|---|
| | 抄造液A（断熱層用） | 抄造液B（熱膨張層用） (Intumescent) | 抄造液C（熱膨張層用） (Intumescent) | 抄造液D（断熱層用） | 断熱層 | 熱膨張層 (Intumescent) 11 |
| 12 セラミック繊維 (Ceramic Fibe) | 6 83 wt% | 7 30 wt% | 8 19 wt% | 9 70 wt% | 10 60~95 wt% | 10~60 wt% |
| 13 セピオライト鉱物 (seopolite) | 5 wt% | 4 wt% | | | 0~10 wt% | 0~10 wt% |
| 14 バーミキュライト鉱物 (vermiculite) | | 54 wt% | 71 wt% | 20 wt% | 0~30 wt% | 30~90 wt% |
| 15 有機結合材 (organic binder) | 12 wt% | | 10 wt% | 10 wt% | 1~20 wt% | 1~20 wt% |
| 16 抄造液濃度 | 1.5 wt% | 1.5 wt% | 1.5 wt% | 1.5 wt% | | |

比較例 17

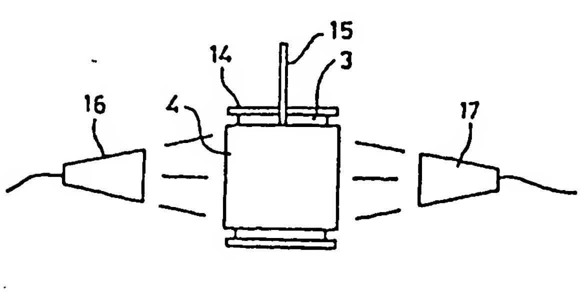
【図5】




【図7】




【図6】




【図8】